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A MINERALOGICAL EXAMINATION OF SILVER FLOTATION CONCENTRATES MADE FROM ZINC LEACH RESIDUES

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A MINERALOGICAL EXAMINATION OF SILVER FLOTATION
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by

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ABSTRACT

Two neutral leach residues and one high acid leach residue from zinc processing circuits were subjected to flotation to produce three silver concentrates. A mineralogical investigation was carried out to characterize the feeds and products and to elucidate the mineral forms of silver. Only one silver occurrence was observed in the neutral leach residues and this was as Ag_2S coatings on sphalerite. Silver sulphide-coated sphalerite was also present in the high acid leach residue although the major occurrence of silver in that feed was a sulphur-silica gel-like material. Silver-bearing jarosite is also a probable silver carrier in that feed. The concentrate produced from the high acid leach residue contained abundant silver as ill-defined masses of $\text{Ag}_2(\text{S},\text{Se})$ bearing some resemblance to the gel-like material in the original feed and as tiny $\text{Ag}_2(\text{S},\text{Se})$ inclusions in elemental sulphur-jarosite clusters. Silver is also probably contained in the jarosite in this concentrate. Abundant silver was evident in the concentrate prepared from the neutral leach residue made in the pilot run; many if not

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most of the sphalerite grains in this concentrate were rimmed with a Pb-Ag sulphide, possibly also containing some Zn and iron. The flotation concentrate made from the neutral leach residue in the CEZ storage pond contained sphalerite rimmed with Ag_2S and $(\text{Cu},\text{Ag})_2\text{S}$; inclusions of these sulphides were also seen in some of the larger sphalerite grains.

EXAMEN MINÉRALOGIQUE DES CONCENTRÉS ARGENTIFÈRES
OBTENUS PAR FLOTTATION DE RÉSIDUS DE LIXIVIATION DU MINÉRAI
DE ZINC

par

J.E. Dutrizac* et T.T. Chen*

RÉSUMÉ

Deux résidus neutres et un résidu très acide de lixiviation provenant des circuits de traitement du zinc ont été soumis à la flottation, de façon à donner trois concentrés argentifères. On a fait une étude minéralogique, pour caractériser les produits de charge et les produits obtenus, et pour élucider le problème des formes minérales de l'argent. On n'a observé qu'une fois l'argent dans les résidus neutres de lixiviation, et cela sous forme d'enduits de Ag_2S recouvrant la sphalérite. On a aussi trouvé de la sphalérite portant un enduit de sulfure d'argent dans le résidu de lixiviation très acide, mais la majeure partie de l'argent se retrouvait dans ce produit de charge sous forme d'un gel composé de soufre et de silice. La jarosite argentifère est aussi probablement un véhicule de l'argent dans ce produit de charge. Le concentré obtenu à partir du résidu de lixiviation très acide contenait de l'argent en abondance sous forme de $\text{Ag}_2(\text{S}, \text{Se})$, plus ou moins similaire au produit de type gel contenu dans le produit de charge initial, et sous forme d'inclusions minuscules de $\text{Ag}_2(\text{S}, \text{Se})$ dans des agrégats de jarosite et de soufre élémentaire. L'argent est probablement présent aussi dans la jarosite de ce concentré. On a mis en évidence

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des quantités abondantes d'argent dans le concentré préparé à partir du résidu de lixiviation neutre fabriqué pendant l'essai à l'échelle semi-industrielle. Un grand nombre, sinon la plupart des particules de sphalérite de ce concentré étaient bordées par un sulfure de Pb et Ag, qui contenait peut-être aussi un peu de Zn et de Fe. Le concentré constitué par flottation à partir du résidu neutre de lixiviation dans le bassin de stockage de la ZEC (Zinc Electrolytique du Canada Limitée) contenait de la sphalérite bordée par Ag_2S et $(\text{Cu},\text{Ag})_2\text{S}$; on a aussi rencontré des inclusions de ces sulfures dans certaines des plus grosses particules de sphalérite.

INTRODUCTION

Silver is present in minor amounts in most commercial zinc concentrates. During processing by the roast-leach-electrowin method, most of the silver reports in the various leach residues; virtually no silver dissolves in the sulphuric acid-zinc sulphate leaching medium despite the relatively high solubility of both Ag_2SO_4 and AgCl in such solutions (1,2). The recovery of silver from the leach residues has traditionally been poor and erratic, with the best success being achieved by the recycle of the residues into a lead smelting circuit coupled with a zinc slag fuming furnace. The use of this practice is, however, clearly limited to those few zinc plants adjacent to conventional lead smelters, and may not be at all possible with the new generation of lead flash smelting furnaces. The recovery of silver values by alternate technologies such as froth flotation would clearly be more universally applicable and could offer processing advantages over the lead smelter route.

In view of the general desirability of developing alternate methods for recovering silver from zinc residues and the recent success of flotation at such installations as Vieille-Montagne's Balen zinc plant, CANMET issued a contract to the Noranda Research Centre to evaluate flotation methods for the recuperation of silver from Canadian zinc plant leach residues. As part of that contract, Noranda Research produced flotation concentrates from both fresh and impounded neutral leach residues and from a high acid leach residue. The purpose of the current CANMET investigation was to complement the corporate contract work by conducting a detailed mineralogical examination of these materials, with special emphasis on their silver mineralogy.

EXPERIMENTAL

Three residues and three flotation concentrates were provided for study. A description of the six samples together with some limited chemical data supplied by the company is presented in Table 1. The samples were reportedly well washed to eliminate soluble salts and were subsequently air dried. All samples were examined "as-received" without any further treatment.

In addition to classical ore microscopy, a variety of mineralogical techniques was used to examine the leach residues and, especially, the flotation concentrates. All samples were examined by X-ray powder diffraction methods to identify the major phases present. A MAC 400 electron microprobe was used in conjunction with the SEM-EDX unit to help locate regions rich in silver. These regions were then subjected to detailed study on the scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) and backscattered electron imagery. Although most of the studies were done using full polished sections of the various materials, some work was also carried out on the loose concentrates to ensure that silver was not being lost during polishing.

RESULTS AND DISCUSSION

4971 - NEUTRAL LEACH RESIDUE FROM THE CEZ STORAGE POND

X-ray diffraction analysis showed this material to consist of zinc ferrite, sphalerite and quartz together with a trace of hematite.

Microscopic examination (Figure 1) indicated relatively coarse composite grains cemented together by an iron hydroxide material which is apparently amorphous and may be mixed with a Fe-Zn sulphate. The fine-grained iron hydroxide phase (medium to dark grey) consists of major iron together with

Table 1 - A description of the six samples provided for mineralogical study

Identifier Number	Description	Chemical Composition (wt.%)				Silver Recovery** Into Concentrate (%)
		Ag*	Zn	Pb	Se*	
4971	Neutral leach residue from the storage pond of Canadian Electrolytic Zinc; this residue was several years old.	0.021	20.4	0.60	-	n.a.
4973	Neutral leach residue from a pilot plant run conducted by Noranda Research.	0.037	22.1	8.33	-	n.a.
4976	High acid leach residue from Kidd Creek Mines, Timmins.	0.13	5.71	5.92	-	n.a.
4987	T-186C, flotation concentrate produced from high acid leach residue.	0.87	-	-	0.35	25%
5009	T-192C, flotation concentrate produced from pilot plant neutral leach residue.	0.98	35.7	3.96	0.04	65%
5028	T-196C, flotation concentrate produced from the neutral leach residue in the CEZ storage pond.	0.25	43.1	-	0.08	44%

* CANMET analysis

** The concentrate from each flotation test was obtained in four fractions; the reported silver recovery applies to only the one (of four) fraction examined.

minor amounts of zinc and traces of Mn, Cu, Al and SO_4 . This phase is abundant but does not give an X-ray diffraction pattern; it is presumably the ferric hydroxide phase formed at moderately high pH values in the neutral leaching step. Zinc ferrite is abundant both as cellular masses (large central light grey mass) and as compact grains (light grey) in the ground-mass. A number of compact grains of hematite are also evident, and these are a slightly darker shade of grey than the zinc ferrite particles. The large centre-right composite grain contains about equal amounts of hematite and zinc ferrite particles. The hematite tends to be pure whereas the ferrite phase contains traces of manganese.

Figure 2 shows the detailed structure of one of the large composite grains cemented together by the iron hydroxide phase. The fibrous grain at the lower-left is an iron silicate containing minor amounts of Al and traces of Zn, Mn, Mg and Ca; a number of grains of Fe-Al silicates and Fe-Al-Mg silicates were identified in this residue. The porous, light grey grain at the lower-centre of the photo is hematite, but most of the other compact, light-grey grains are zinc ferrite. Figure 3 illustrates another field of view of one of the composite grains which is again cemented together by an iron hydroxide phase. In this photograph, the dark grey central grain is quartz and the medium grey oval grains at the lower-centre-left are manganese oxide (MnO_2 ?) containing minor Fe and traces of Cu and Zn. The large light grey grain at the centre-left is zinc ferrite containing a trace of copper.

Other phases detected during the examination of this residue included pyrite, sphalerite and a Zn-Fe sulphate. No silver minerals or silver-bearing phases were found in this residue which contained 210 ppm Ag.

4973 - NEUTRAL LEACH RESIDUE FROM THE PILOT PLANT RUN

X-ray diffraction analysis showed this residue to consist mostly of zinc ferrite and lead sulphate.

Microscopically, this neutral leach residue was considerably different from the pond residue examined above in that it is more fine grained and is entirely lacking in the large aggregates cemented by iron hydroxide. Figure 4 presents a general view of this leach residue, and it is clear that it consists mostly of particles less than 10 μm although a few larger grains are also evident. Near the centre of the field is a large medium grey grain of iron-bearing sphalerite and similar grains were evident in most of the fields examined. The slightly darker, tiny compact grains forming the majority of the field are zinc ferrite. The light grey to white particles are lead sulphate, and these are generally $<5 \mu\text{m}$ although a large (15 μm) PbSO_4 spherical cluster is evident in the lower-left corner. The somewhat nebulous medium grey mass associated with this PbSO_4 cluster is a zinc-iron sulphate containing some lead and traces of Si, Cu and Mn. Trace amounts of hematite, magnetite and pyrite were also seen in this residue.

Figure 5 shows the detailed structure of the pilot plant neutral leach residue, and this figure is of some significance since it illustrates the only silver-bearing grain detected. In this field, the small ($<10 \mu\text{m}$) medium grey compact grains are zinc ferrite and the small white particles are PbSO_4 . The large central grain is iron-bearing sphalerite, and the grey zone ($\sim 2 \mu\text{m}$) at the bottom tip of the sphalerite grain is Ag_2S . Clearly, this one silver particle is not adequate to account for all of the 370 ppm Ag contained in this residue, but it does indicate how silver occurs in this material.

4976 - HIGH ACID LEACH RESIDUE

X-ray powder diffraction analysis showed this residue to consist predominantly of a jarosite-type compound, lead sulphate and sphalerite.

Microscopic study indicated the residue to be extremely fine grained, with most particles being $<10\text{ }\mu\text{m}$ in diameter. Figure 6 presents a general view of the residue and the fine-particle sizes are readily discernible. In this photo, the medium grey, fine grained mass constituting the majority of the field of view is a jarosite-type compound (likely a Pb-K-Zn-bearing sodium jarosite), and the white grains are sphalerite. The medium, compact grains ($\sim 10\text{ }\mu\text{m}$) are hematite or zinc ferrite, often intimately associated with the jarosite. Study of this residue also indicated minor to trace amounts of quartz and sphalerite ($\sim 3\text{ }\mu\text{m}$) as well as traces of chalcopyrite, pyrite, gypsum, a manganese sulphide (?) and a tin sulphide.

Two forms of silver were identified in this residue and a third (trace Ag substitution in the jarosite-type compounds) likely exists as well (3). The major occurrence of silver was as a poorly defined gel-like layer, commonly situated at the edge of a hole or pit or at the polished surface. Figure 7a illustrates the general morphology of these gel-like layers, and Figure 7b shows the relative silver (AgL_{α} X-ray map) distribution in the gel. The gel-like phase (central white to light grey mass in Figure 7a) consistently indicated major sulphur and silicon together with minor Ag and Fe, and traces of Zn, Pb, Sn and Al. It is felt that the gel-like phase consists essentially of elemental sulphur and a silica gel; the method by which silver is incorporated in such material is not known but it is likely present as fine Ag_2S particles. The second identified form of silver was thin coatings of Ag_2S on the edges of iron-bearing sphalerite grains. The silver sulphide always contained minor to trace amounts of Pb as well as occasional traces

of Se. Unfortunately, the Ag_2S layer was too thin and too intimately associated with other phases for a definitive electron microprobe analysis. The amounts of silver observed, when considered in the light of the probable Ag content of the jarosite phase, are likely sufficient to account for the 1,300 ppm Ag in this residue.

4987 - FLOTATION CONCENTRATE FROM THE HIGH ACID LEACH RESIDUE

X-ray powder diffraction analysis of this concentrate indicated a jarosite-type compound, sphalerite, elemental sulphur and possibly some lead sulphate. The presence of elemental sulphur was confirmed by X-ray diffraction analysis of grains removed from the powder mounts.

Microscopic examination of polished sections of this flotation concentrate indicated a very fine-grained texture with most particles being $<2 \mu\text{m}$ in size. Figure 8 illustrates a general view of this material and clearly shows the fine grain size of most of the particles. The majority of the field of view (medium grey) consists of jarosite-type compounds showing major iron and sulphur together with minor amounts of Na, Pb, K and Zn, and traces of Ag, Si, Al, Se, Ba and Sn. The jarosite-type compound is likely a Pb-K-Zn-bearing sodium jarosite. It is felt that the Ag, Al and Se are associated with the jarosite but that the other elements are present as discrete impurity grains (3). The fine particle sizes in this material, do not permit a definitive clarification of the elements substituted in the jarosite as opposed to those elements intimately mixed with the jarosite phase as tiny impurity grains. A previous study (3) has, however, shown Ag substitution in the jarosite contained in a similar residue from Kidd Creek Mines. The bright white, compact grains in Figure 8 are iron-bearing sphalerite, and the spherical black spots (e.g., upper right corner) are elemental sulphur associated with jarosite.

Elemental sulphur does not polish particularly well and it commonly lifts out of the section during polishing. To try to show the elemental sulphur better, a loose powder mount of this concentrate was prepared, and this is shown in Figure 9. The light grey spherical clusters (2-50 μm) are elemental sulphur containing traces of Fe, Zn and Si. The sulphur clusters are frequently intimately mixed with jarosite-type compounds. The abundance of the sulphur clusters as shown in the loose powder mount would not be inferred from an examination of the polished section of this flotation concentrate (Fig. 8). Figure 10 shows the detailed structure of one of the sulphur-jarosite clusters, and it is evidently porous and composed of a number of still smaller particles.

Other compounds observed during the general study of this concentrate, in either polished section or loose powder mounts, include minor amounts of chalcopyrite and zinc ferrite as well as traces of quartz, SnO_2 (cassiterite), hematite and BaSO_4 (barite).

This concentrate contains 0.87% Ag and over 25 separate Ag-bearing grains were examined during the study of this material. Two (but possibly closely related) forms of silver were identified and it is also likely that silver is substituted to a limited extent in the jarosite crystals. Analysis of masses of jarosite crystals (individual crystals are too small for individual analysis) indicated traces of silver but, of course, there is no way of knowing for sure that the silver is actually incorporated in the Pb-K-Zn-bearing sodium jarosite lattice.

One major type of occurrence of silver was as ill-defined masses of a silver sulphide phase closely associated with minor Si and traces of Fe, Zn, Pb and Al. This material was always associated with a hole or the edge of a hole and bore some resemblance to the gel-like particles detected in the high

acid leach residue. Selenium was always closely associated with silver in this mode of occurrence and the actual silver compound is likely $\text{Ag}_2(\text{S,Se})$. Figure 11 illustrates one of these masses of $\text{Ag}_2(\text{S,Se})$ where the silver phase is the large ($\sim 25 \mu\text{m}$) medium grey mass showing a central hole. The ill-defined mass shows major sulphur and silver, minor silicon and traces of Fe, Se and Zn. The mass of silver sulphide is surrounded by fine crystals of jarosite (medium grey) and small grains of sphalerite (white).

Figure 12a illustrates another of these $\text{Ag}_2(\text{S,Se})$ masses which is clearly associated with a large crack. Figure 12b illustrates the relative concentration of silver (AgL_{α} X-ray map). The silver-bearing region consisted of $\text{Ag}_2(\text{S,Se})$ with minor iron and traces of Zn, Si, Pb and Al. The small rings (white) in the lower-right quadrant consist mostly of sulphur containing minor silver and silicon together with traces of Fe, Zn, Al, Pb and Se. These sulphur rings seem to be joined to the central mass of $\text{Ag}_2(\text{S,Se})$. Figure 13 illustrates the detailed structure of another $\text{Ag}_2(\text{S,Se})$ mass. It is evident that the silver sulphide is lacking in crystal features and that it is rough and irregular; it has the features of a precipitate.

The second major type of silver occurrence was as tiny $\text{Ag}_2(\text{S,Se})$ inclusions in the elemental sulphur-jarosite clusters. Examination of the sulphur in the loose powder mounts (Fig. 9) commonly indicated $\text{Ag}_2(\text{S,Se})$ particles as is evident in Figures 14 and 15 where the sulphur-jarosite masses are the medium grey phase and the $\text{Ag}_2(\text{S,Se})$ is white. The silver sulphide particles in the sulphur-jarosite masses are $\sim 2 \mu\text{m}$ in size and also seem to be selenium-bearing. The sulphur-jarosite masses contain minor Si and Fe as well as trace quantities of Zn, Pb, Al, Ba and Sn. Chlorine was occasionally detected with Ag in the loose powder mounts, but this is felt to originate

from the mounting glue used to attach the powder to the stage and not to be due to silver chloride. Silver sulphide rimmed sphalerite was present in the leach residue, but **was not seen** in this concentrate which contains only 25% of the silver in the original feed (Table 1).

5009 - FLOTATION CONCENTRATE FROM THE PILOT PLANT NEUTRAL LEACH RESIDUE

The concentrate prepared from the pilot plant neutral leach residue was shown by X-ray powder diffraction analysis to consist of major sphalerite and zinc ferrite together with a trace amount of quartz.

Microscopic study of this concentrate showed it to consist (Figure 16) of major iron-bearing sphalerite as both fine and coarse grains (light grey) in a matrix of fine-grained zinc ferrite (dark grey). Also present were occasional grains of quartz, pyrite and chalcopyrite. Most of the sphalerite grains are rimmed by a sulphide phase containing Ag and Pb together with lesser amounts of Fe and Zn.

This concentrate contains 0.98% Ag and abundant silver was detected mineralogically in this sample. The silver seemed to occur exclusively as a compact to diffuse rim on the sphalerite grains, especially the medium to small size grains ($\leq 10 \mu\text{m}$); most of these smaller particles were rimmed by the Ag-bearing sulphide and many of the larger sphalerite grains were likewise coated. Figure 17 shows a small and a medium sized grain of iron-bearing sphalerite (medium grey) completely rimmed by the Ag-bearing sulphide (white to light grey). The sulphide rim varies in thickness from $\sim 1 \mu\text{m}$ to several microns. Figure 17b presents a AgL_{α} X-ray map showing the relative distribution of silver about the two grains, and Figure 17c illustrates the corresponding X-ray map (PbL_{α}) for lead. It is clear that the rims are enriched in lead and silver, and that there is a general correlation between

the lead and silver contents. SEM-EDX analysis of many of the rims indicated them to consist of a Pb-Ag sulphide containing minor amounts of Zn and traces of Fe. The Zn and Fe may represent part of the underlying sphalerite particle. The mineralogical equivalent of the Pb-Ag sulphide is not known.

Although the Pb-Ag sulphide appears single phase, significantly, Pb-Ag sulphides have not been reported in the mineralogical literature and the possibility exists that the rims may be an intimate mixture of PbS and Ag_2S .

Figure 18 indicates several medium to small iron-bearing sphalerite particles (medium grey) all of which are extensively rimmed by compact layers of Pb-Ag sulphide (white to light grey). Again, it must be emphasized that most of the sphalerite grains in this flotation concentrate are rimmed by this Ag-bearing sulphide phase.

5028 - FLOTATION CONCENTRATE FROM THE NEUTRAL LEACH RESIDUE IN THE CEZ STORAGE POND

X-ray powder diffraction analysis showed this concentrate to consist of major amounts of sphalerite and zinc ferrite.

Microscopic study (Figure 19) showed the concentrate to consist generally of fairly large sphalerite particles (light grey) in a fine matrix (medium grey) composed of major zinc ferrite and tiny sphalerite grains together with minor hematite and trace amounts of pyrite, quartz, chalcopyrite and silicates. A large silicate grain ($5 \times 20 \mu\text{m}$, medium grey) is situated at the right-centre of the field shown in Figure 19. A porous hematite particle (light to medium grey, $\sim 15 \mu\text{m}$) is found in the lower-left corner, and its texture suggests a roaster product, likely a calcined pyrite grain.

This concentrate assayed 0.25% Ag, and many silver-bearing grains were identified. In every instance, the silver seemed to be present as Ag_2S or $(\text{Cu},\text{Ag})_2\text{S}$ on the edges of sphalerite grains (especially the smaller particles) and as inclusions within larger sphalerite particles.

Figure 20a shows a larger sphalerite particle (light grey), the upper surface of which (porous, medium grey) is covered with Ag_2S containing a trace of copper. The relative concentration of silver along this face of the sphalerite grain is shown in Figure 20b.

Figure 21a is a smaller sphalerite grain (white) shown at high magnification. This particle contains a rim of $(\text{Ag,Cu})_2\text{S}$ that is $<1\text{ }\mu\text{m}$ thick and is clearly quite diffuse as evidenced by the AgL_α X-ray distribution map shown in Figure 21b. A high copper content is associated with the silver at the bottom-centre edge of the sphalerite grain. The complete encapsulation of the sphalerite coupled with the diffuse nature of the $(\text{Ag,Cu})_2\text{S}$ layer supports the contention that the silver-bearing sulphide has been precipitated onto the surface of the sphalerite grain.

Figure 22a illustrates a large sphalerite grain (white or light grey) surrounded by a fine mixture of zinc ferrite and sphalerite (medium grey). In the centre of the sphalerite grain is a light grey mass about $10\text{ }\mu\text{m}$ in size which seems to consist of silver-bearing Cu_2S ; associated with this Cu_2S mass is a hole (black) which is lined with copper-bearing Ag_2S . Figure 22b shows the relative distribution of silver in the sphalerite inclusion and Figure 22c indicates the corresponding relative copper concentration.

CONCLUSIONS

Two neutral leach residues and one high acid leach residue from zinc processing circuits were subjected to flotation to produce three silver concentrates. These six samples were examined mineralogically to determine their phase characteristics and to elucidate the mineral forms of silver.

The neutral leach residue from the CEZ storage pond consisted of zinc ferrite, sphalerite, quartz and hematite, often cemented together by an amorphous iron hydroxide possibly containing a Fe-Zn sulphate; no silver-bearing minerals were detected in this residue. The concentrate prepared from the pond residue consisted of major sphalerite and zinc ferrite together with minor amounts of hematite and traces of pyrite, quartz, chalcopyrite and silicates. This concentrate contained abundant silver as rims of Ag_2S or $(\text{Cu},\text{Ag})_2\text{S}$ on sphalerite; inclusions of these sulphides in the larger sphalerite grains were also seen.

The neutral leach residue from a pilot plant run consisted of fine-grained zinc ferrite, lead sulphate and sphalerite together with traces of hematite, magnetite and pyrite. Silver-bearing material was detected in this residue as an Ag_2S coating on one sphalerite grain. The flotation concentrate made from this residue consisted of sphalerite and zinc ferrite together with a trace of quartz. Many if not most of the sphalerite grains were rimmed by a continuous layer of Pb-Ag sulphide which may be a mixture of PbS and Ag_2S although the identity of this phase is not clear.

A high acid leach residue from Kidd Creek Mines was also examined and was found to consist of a jarosite-type compound, lead sulphate and sphalerite with minor amounts of hematite and zinc ferrite as well as traces of chalcopyrite, pyrite and gypsum. There is some evidence that the jarosite is silver-bearing, and silver was clearly evident in masses of sulphur-silica gel and as thin coatings on sphalerite. The silver was always closely associated with Se and was likely present as $\text{Ag}_2(\text{S},\text{Se})$. The concentrate prepared from the high acid leach residue consisted of a jarosite-type compound (likely Ag-bearing), sphalerite, elemental sulphur and possibly some lead sulphate together with minor to trace amounts of chalcopyrite, zinc

ferrite, quartz, cassiterite and barite. Silver was frequently detected, either as ill-defined masses of selenium-bearing silver sulphide closely associated with minor Si or as $\text{Ag}_2(\text{S}, \text{Se})$ particles in elemental sulphur-jarosite clusters.

In this study, silver was generally present as the sulphide which was intimately associated with gel-like masses, sphalerite or other sulphides. Previous work suggests that silver is also contained in the jarosite phase seen in the high acid leach products. Chlorine was rarely detected and, on those occasions, it seemed to originate from glues, mounting media, etc., and not from silver chloride. The abundance of silver-rimmed sphalerite in some of the concentrates coupled with its comparative absence in the respective residues might indicate some mobility/concentration of silver during the actual flotation process.

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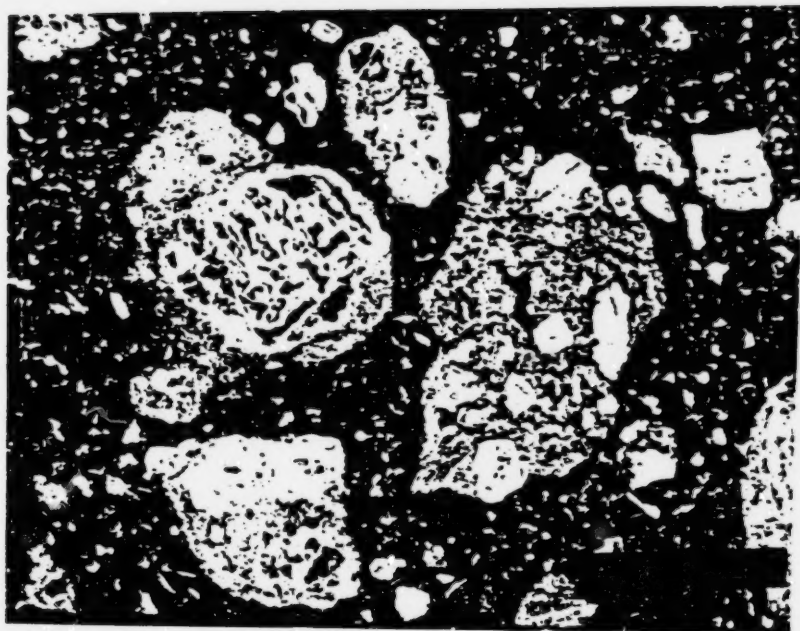


Fig. 1 - Backscattered electron micrograph of the neutral leach residue from the CEZ pond that illustrates the general aggregated morphology of the material.



Fig. 2 - Secondary electron micrograph of one of the composite grains in the neutral leach residue from the CEZ pond.



Fig. 3 - Backscattered electron micrograph of another composite grain in the neutral leach residue from the CEZ pond.

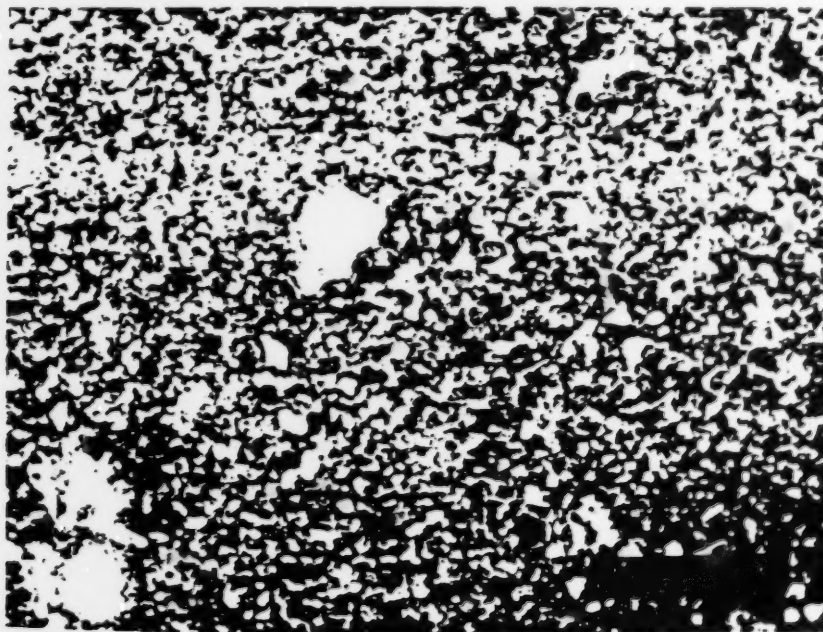


Fig. 4 - Backscattered electron micrograph giving a general view of the neutral leach residue from the Noranda pilot plant run.

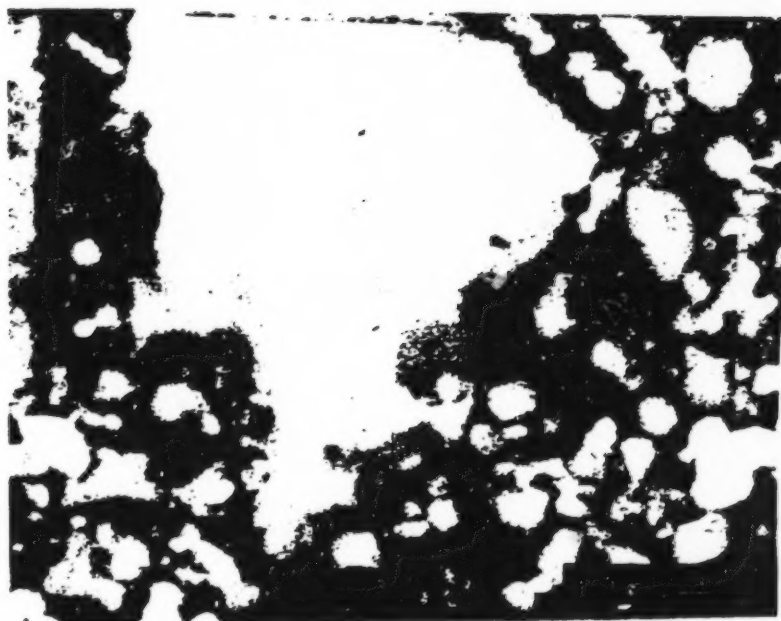


Fig. 5 - Backscattered electron micrograph of a large sphalerite particle in the pilot plant neutral leach residue that has a tiny zone of Ag_2S at the extreme lower tip.

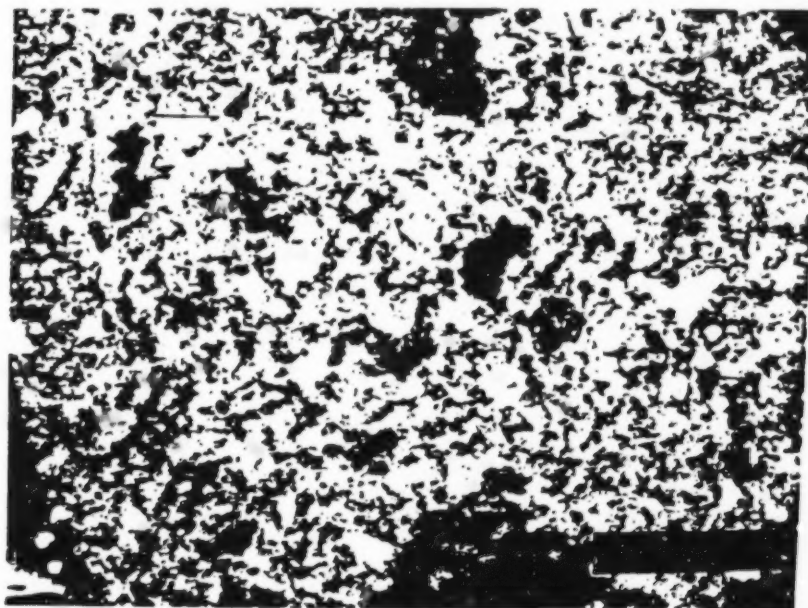


Fig. 6 - Backscattered electron micrograph of the high acid leach residue from Kidd Creek Mines that illustrates the general features of this material.

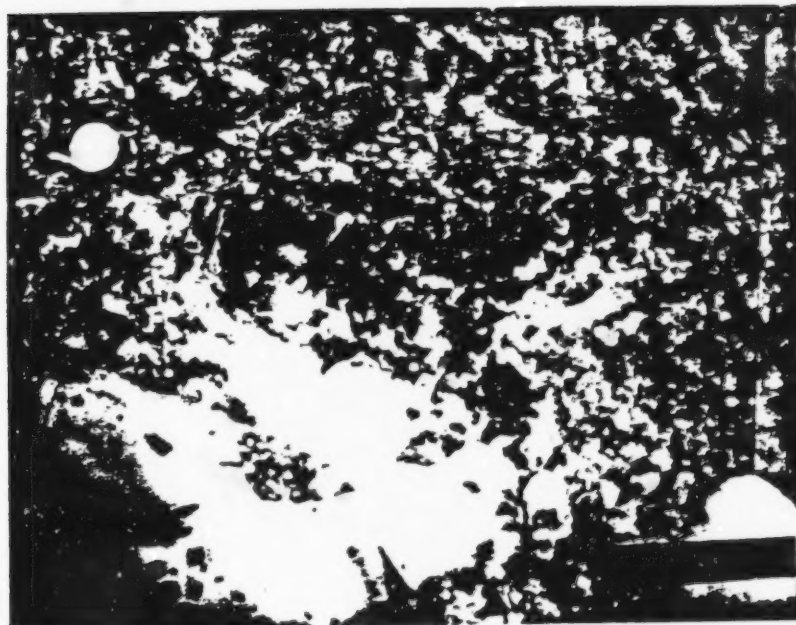


Fig. 7a - Secondary electron micrograph illustrating a Ag-bearing gel-like mass associated with a hole in the high acid leach residue from Kidd Creek Mines.

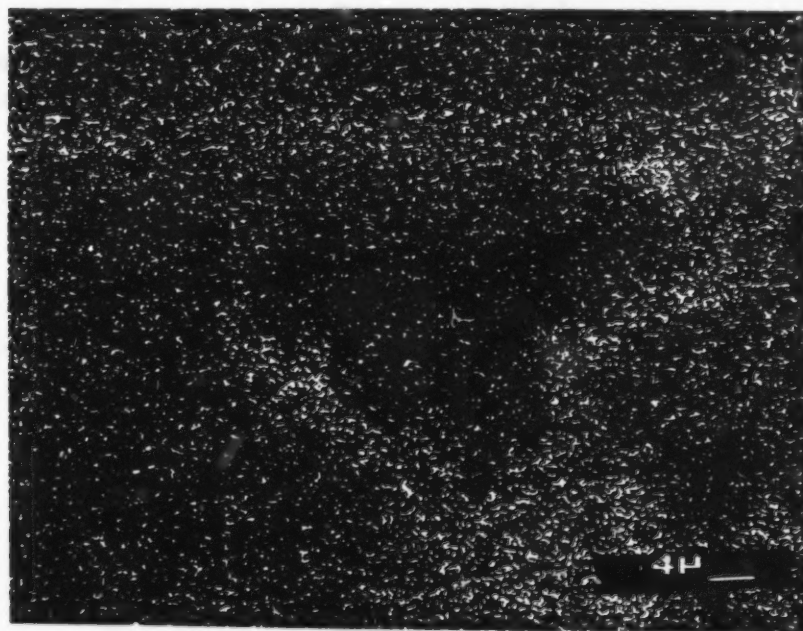


Fig. 7b - $\text{AgL}\alpha$ X-ray map showing the relative concentration of silver in the gel-like mass of Fig. 7a.

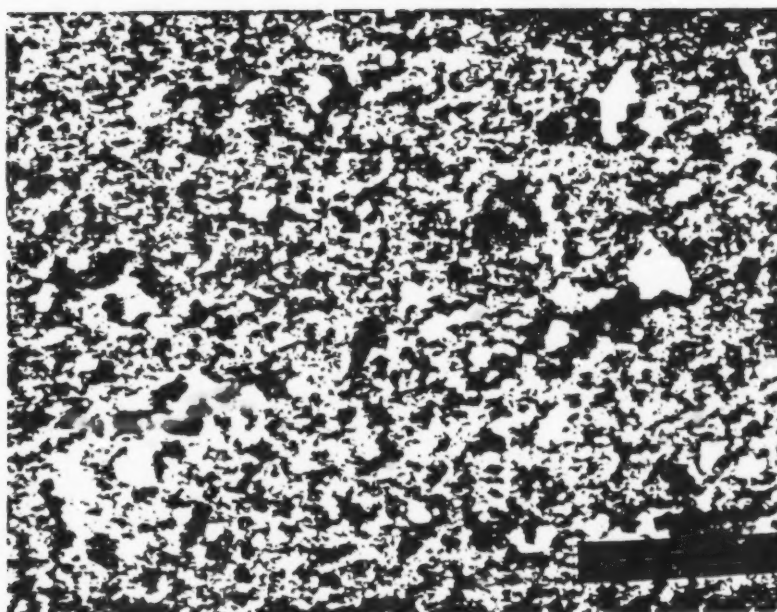


Fig. 8 - Backscattered electron micrograph showing the general characteristics of the flotation concentrate made from the high acid leach residue.

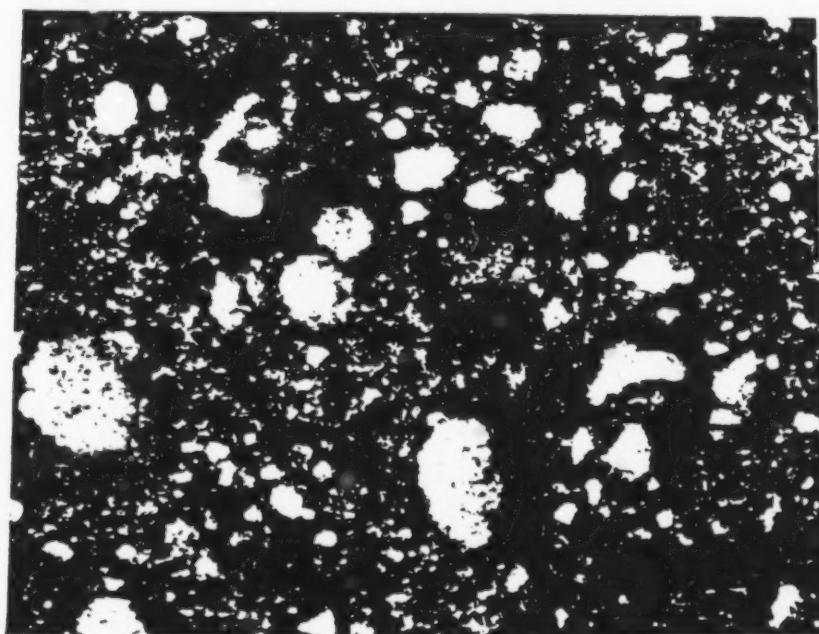


Fig. 9 - SEM micrograph of the flotation concentrate (in loose powder mount) made from the high acid leach residue, and showing abundant coarse grained sulphur clusters (light grey).



Fig. 10 - SEM micrograph of a sulphur cluster in the loose powder mount of the concentrate made from the high acid leach residue.



Fig. 11 - Backscattered electron micrograph of an ill-defined $\text{Ag}_2(\text{S,Se})$ mass in the concentrate made from the high acid leach residue.



Fig. 12 - a) Secondary electron micrograph of a mass of $\text{Ag}_2(\text{S},\text{Se})$ closely associated with a crack.

b) AgL_α X-ray map showing the relative distribution of silver in this particle.



Fig. 13 - Secondary electron micrograph showing the detailed structure of a mass of $\text{Ag}_2(\text{S},\text{Se})$.

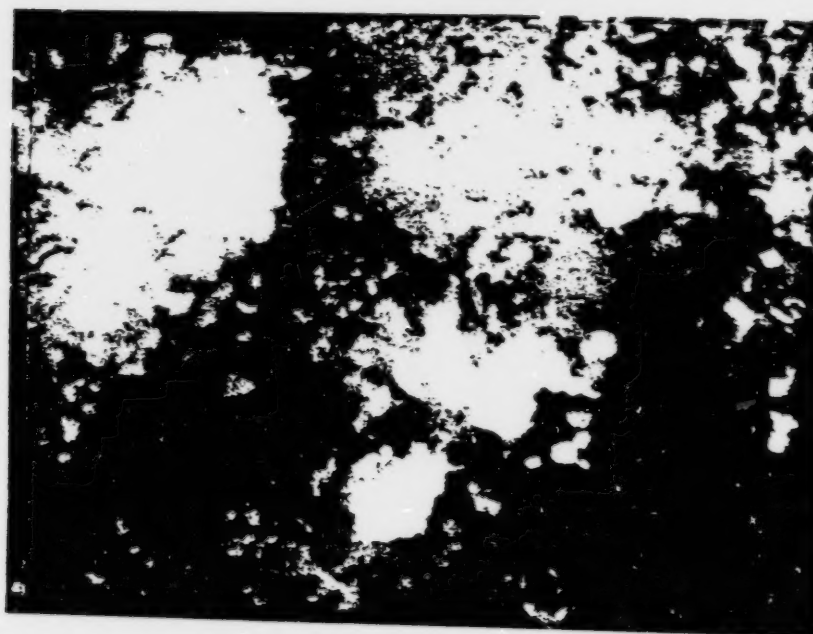


Fig. 14 - Backscattered electron micrograph of tiny $\text{Ag}_2(\text{S},\text{Se})$ particles (white) in a sulphur-jarosite cluster (grey). Loose powder mount.

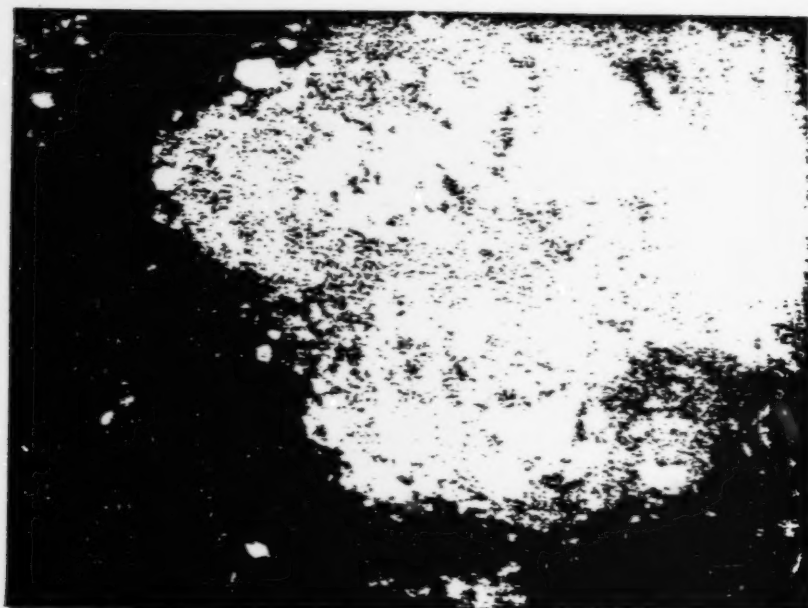


Fig. 15 - Backscattered electron micrograph of small $\text{Ag}_2(\text{S},\text{Se})$ grains (white) in large sulphur-jarosite clusters (grey). Loose powder mount.

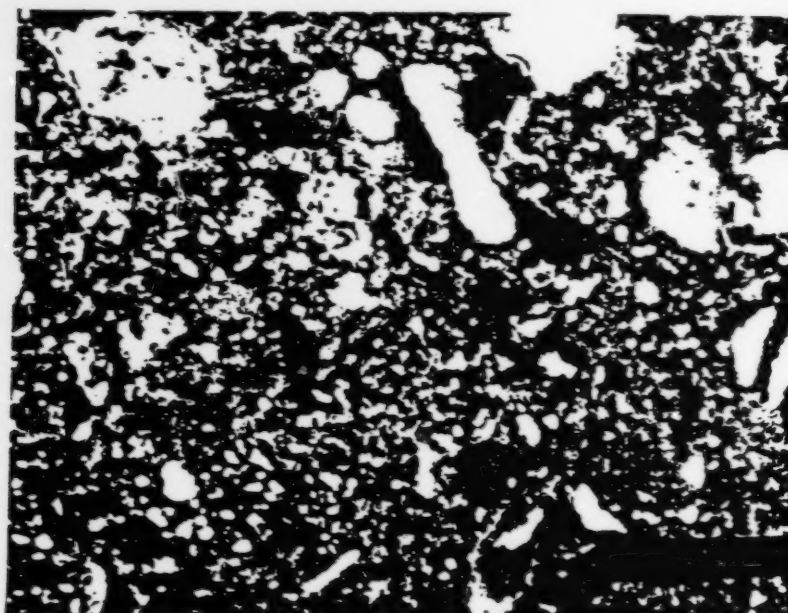


Fig. 16 - Backscattered electron micrograph showing a general view of the concentrate made from the pilot plant neutral leach residue.

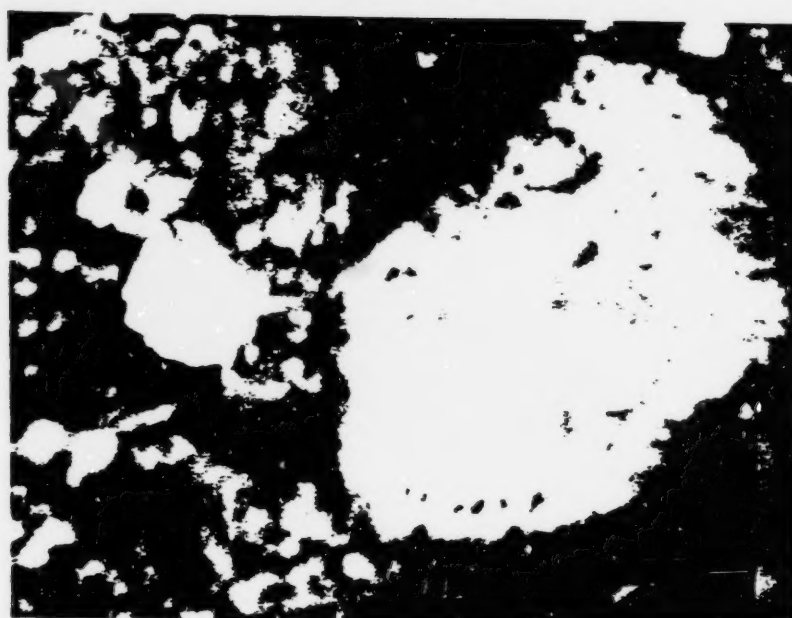


Fig. 17 - a) Backscattered electron micrograph illustrating sphalerite particles (medium grey) rimmed by Pb-Ag sulphide (white) in the concentrate made from the pilot plant neutral leach residue.

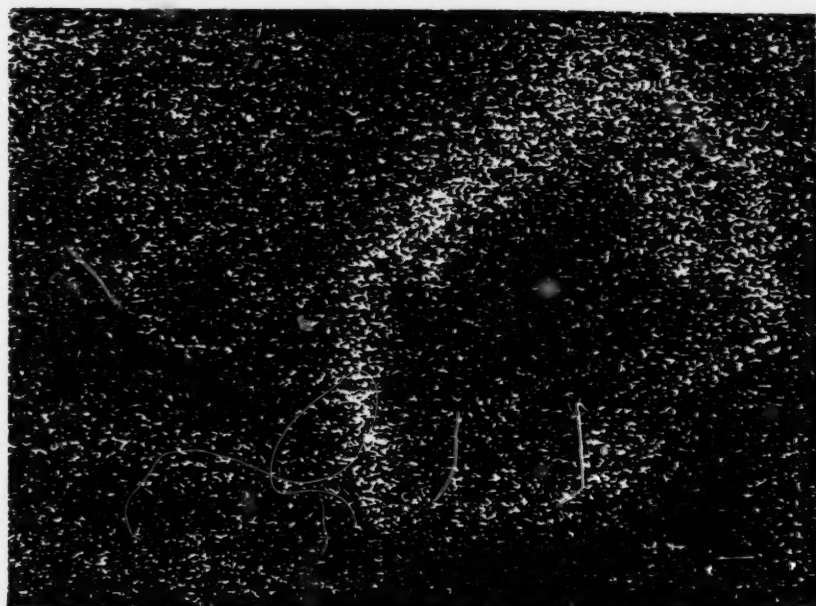


Fig. 17 - b) AgL_{α} X-ray map showing the relative distribution of silver in Fig. 17a.

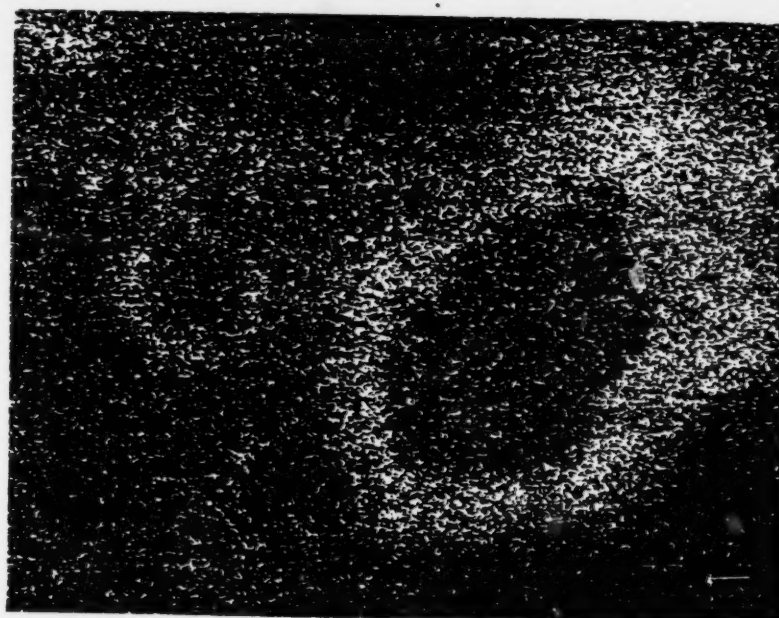


Fig. 17 - c) PbL_{α} X-ray map showing the relative distribution of lead and its close association with silver in Fig. 17a.

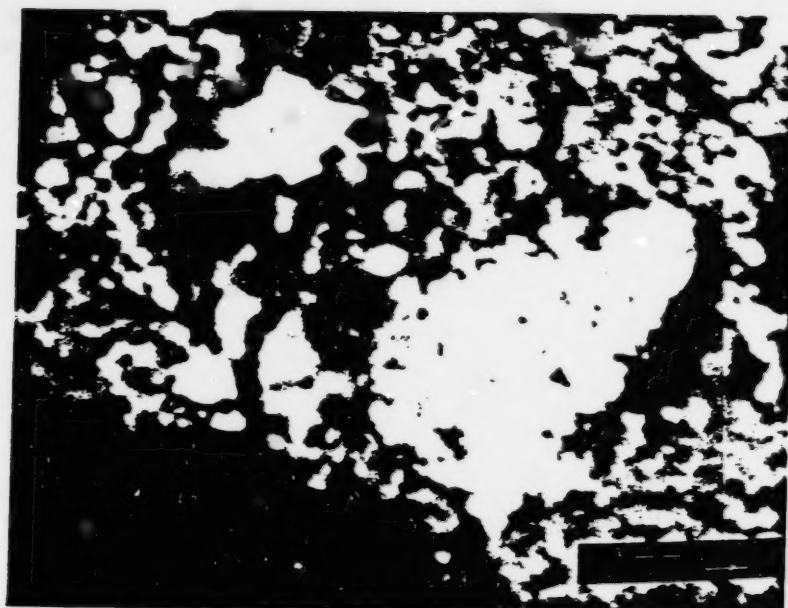


Fig. 18 - Backscattered electron micrograph of several smaller sphalerite grains (medium grey) all rimmed by Pb-Ag-sulphide in the concentrate made from the pilot plant neutral leach residue.

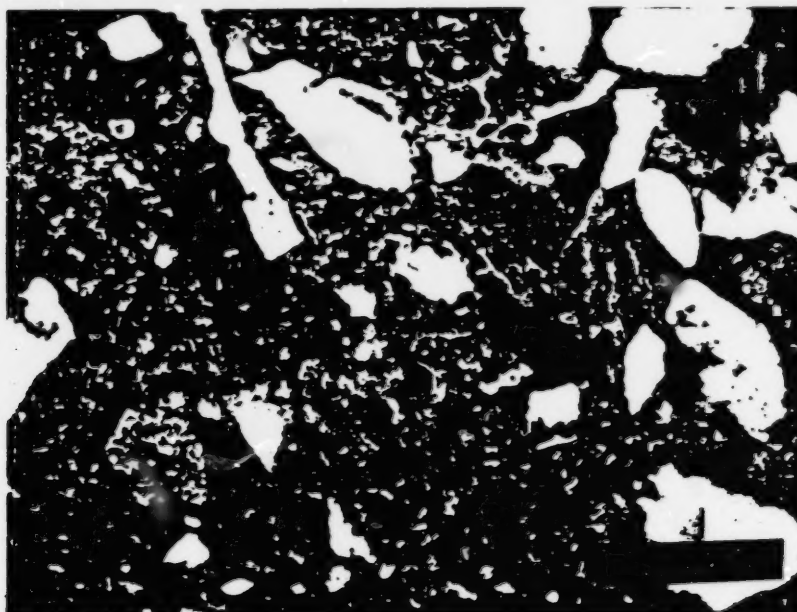


Fig. 19 - Backscattered electron micrograph showing a general view of the concentrate made from the neutral leach residue in the CEZ storage pond.

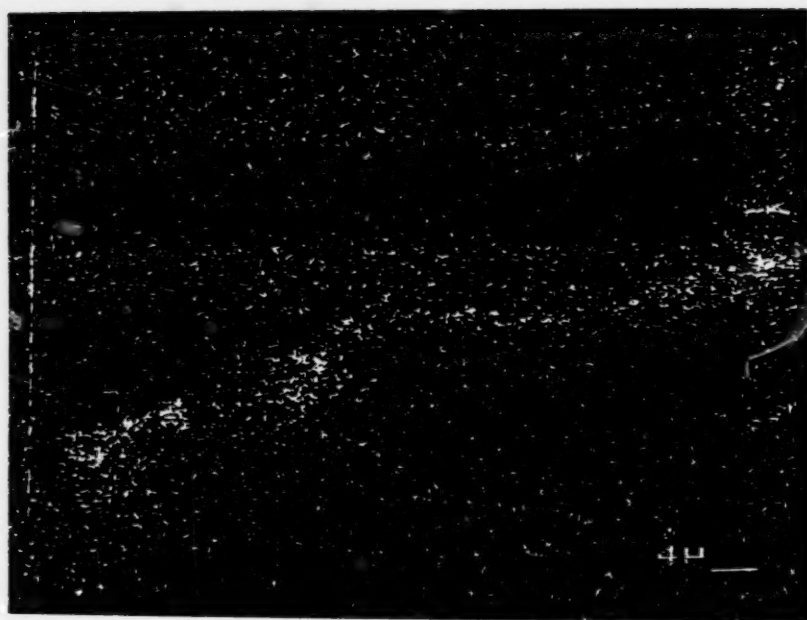


Fig. 20 - a) Backscattered electron micrograph of a sphalerite grain in the neutral leach residue from the CEZ pond. The upper surface is coated with Ag_2S (whiter).

b) AgL_α X-ray map showing the relative distribution of silver and its concentration at the top of the grain.

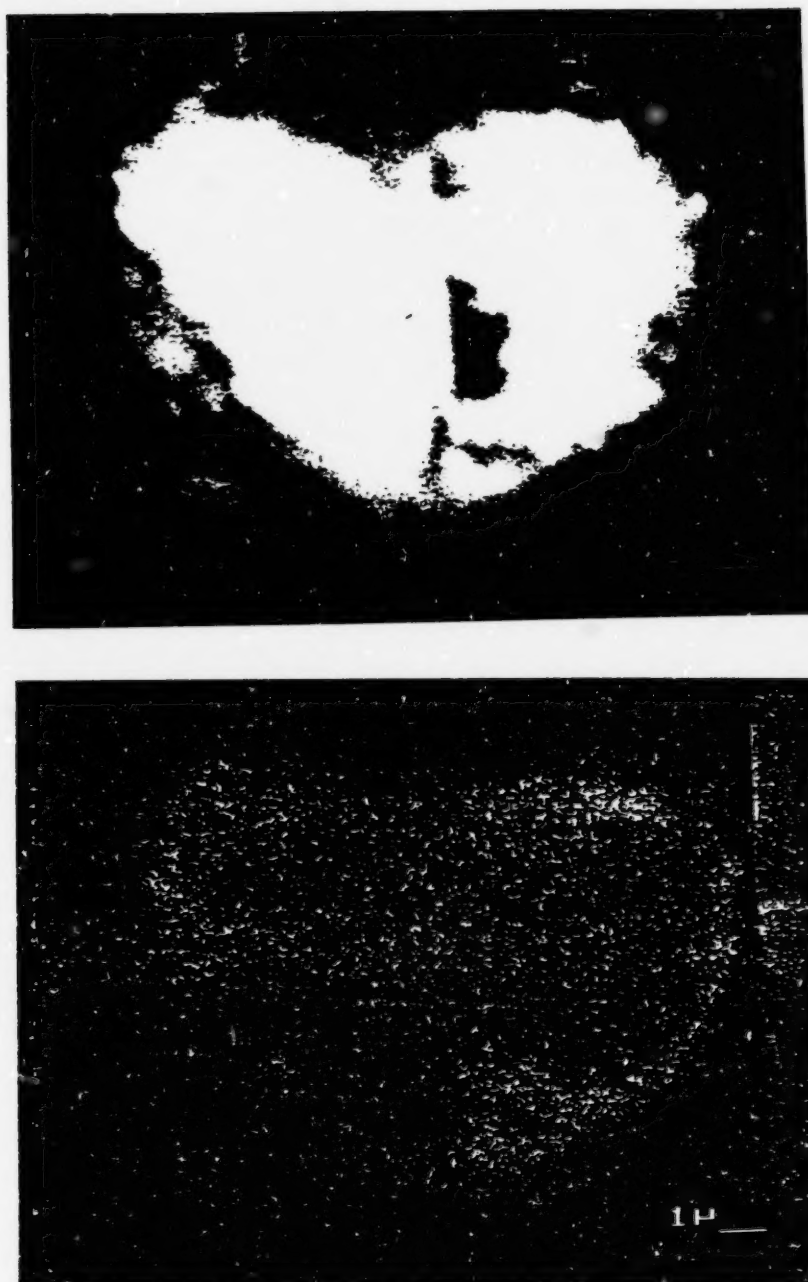


Fig. 21 - a) Backscattered electron micrograph showing a small sphalerite grain rimmed by $(\text{Cu},\text{Ag})_2\text{S}$ (light spots, porous) in the concentrate prepared from the neutral leach residue in the CEZ pond.
b) AgL_γ X-ray map showing the diffuse distribution of silver about the sphalerite grain.

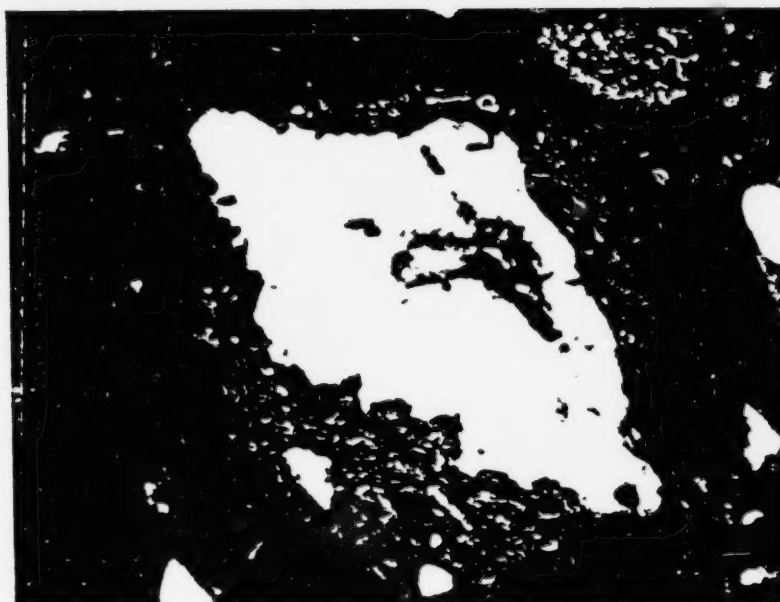


Fig. 22 - a) Backscattered electron micrograph of a large sphalerite grain (light grey) in the concentrate made from the neutral leach residue in the CEZ storage pond. In the centre of the grain is a composite inclusion of silver-bearing Cu₂S (medium grey) and copper-bearing Ag₂S.



Fig. 22 - b) AgL_{α} X-ray distribution map showing the concentration of silver in the composite inclusion.

c) CuK_{α} X-ray map illustrating the concentration of copper in the composite inclusion.

